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FORM PTO-1390) (REV. 9-2001) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER
635.40828X00 filed December 14, 2001

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)
10/018091

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/CH00/00268	**May 16, 2000**	**June 14, 1999**

TITLE OF INVENTION
DISPOSAL OF RADIOACTIVE MATERIALS

APPLICANT(S) FOR DO/EO/US
DOEHRING, LOTHAR TRESS, GERHARD

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)))
   a. ☐ is transmitted hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office(RO/US)
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☒ A substitute specification.
16. ☒ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information: **Figs. 1-6; Credit Card Payment Form; PCT Request Form; International Publication No. WO 00/77793; International Preliminary Examination Report w/amended sheets**

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U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/018091	INTERNATIONAL APPLICATION NO. PCT/CH00/00268	ATTORNEY'S DOCKET NUMBER 635.40828X00

21. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492(a) (1) - (5)):

☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1040.00**

☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$890.00**

☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$740.00**

☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$710.00**

☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**

				CALCULATIONS	PTO USE ONLY
ENTER APPROPRIATE BASIC FEE AMOUNT =				$890.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)). ☐ 20 ☐ 30				$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	$	
Total Claims	23- 20 =	3	x **$18.00**	$54.00	
Independent Claims	3- 3 =	0	x **$84.00**	$	
MULTIPLE DEPENDENT CLAIMS(S) (if applicable)			+ **$280.00**	$	
TOTAL OF ABOVE CALCULATIONS =				$944.00	
☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by ½. +				$	
SUBTOTAL =				$944.00	
Processing fee of **$130.00** for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(f)). ☐ 20 ☐ 30				$	
TOTAL NATIONAL FEE =				$944.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$	
TOTAL FEES ENCLOSED =				$944.00	
				Amount to be refunded:	$
				charged:	$

a. ☐ A check in the amount of $____ to cover the fees is enclosed.

b. ☐ Please charge my Deposit Account No. 01-2135 in the amount of $____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposition Account No. **01-2135**. A duplicate copy of this sheet is enclosed.

d. ☒ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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SIGNATURE

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NAME

28,577

REGISTRATION NO.

10/018091

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635.40828X00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): L. DOEHRING ET AL.

Serial No.: New Application

Filed: December 14, 2001

For: DISPOSAL OF RADIOACTIVE MATERIALS

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

December 14, 2001

SIR:

The following amendments and remarks are submitted at the time of filing the application.

IN THE SPECIFICATION

An Abstract of the Disclosure is submitted herewith on a separate sheet. It is requested that the Abstract be added to the application specification.

Please replace the original specification with the attached Substitute Specification. A marked-up copy of the Substitute specification with changes

from the original shown by underlining for additions, and bracketing for deletions, is also enclosed.

IN THE CLAIMS

Please cancel claims 1-16 without prejudice or disclaimer and add the following new claims 17-39 therefor:

17. Method for disposal of radioactive materials, comprising providing a binder/aggregate mixture for producing at least one of an embedding material, a mortar, and a casting resin, wherein the aggregate is partially substituted by at least one radioactive material to be disposed of, and wherein the at least one radioactive material to be disposed of is nearly devoid of ultrafine components.

18. Method according to claim 17, wherein the proportion of fines in the radioactive material having a grain size of < 250 μm amounts to less than 30% of the weight of the material to be disposed of.

19. Method according to claim 18, wherein the proportion of fines of < 250 μm is less than 15 wt.% of the material to be disposed of.

20. Method according to claim 17, wherein the mixture includes a hydraulic binder.

21. Method according to claim 17, wherein the mixture comprises a reaction resin as a binder.

22. Method according to claim 17, wherein the at least one radioactive material is used as the aggregate in the mixture and partially replaces a filler in the mixture, and wherein the mixture further comprises a mortar or casting compound for embedding or encapsulating other materials to be disposed of in a receptacle or container.

23. Method according to claim 17, wherein the at least one radioactive material includes reactor graphite which is broken up into small pieces and wherein the mixture further includes a hydraulic binder and other additives as a mortar or casting compound formulation for embedding or encapsulating other radioactive and/or toxic materials to be disposed of.

24. Method according to claim 17, wherein the at least one radioactive material includes radioactive reactor graphite which is wet-ground to a grain size

of < 60 mm and then is mixed together with at least one hydraulic binder for the production of a mortar or embedding compound formulation.

25. Method according to claim 17, wherein the proportion of fines of < 200 μm grain size of the material to be disposed of amounts to less than 20% by weight of the material to be disposed of.

26. Method according to claim 17, wherein the mixture further comprises formulation additives for increasing the flowability, filling ratio, corrosion resistance, resistance to aging, resistance to leaching, and surface wettability of the at least one of the embedding material, mortar and casting resin produced by the mixture.

27. Method according to claim 17, wherein the filling ratio of the at least one of the embedding material, mortar and casting resin produced by the mixture with radioactive material is higher than the filling ratio when conventional aggregates such as sand, gravel and/or additives such as clinoptilolith, micropoz, powdered limestone, quartz powder, and others in the mixture are not substituted for by the radioactive material.

28. Method according to claim 17, wherein the mixture includes sulfate-resistant and/or corrosion-resistant cement as a binder.

29. Method according to claim 17, wherein the material to be disposed of is radioactive graphite to which a wetting agent has been added while crushing or grinding the graphite.

30. Casting compound containing as a binder recipe at least one hydraulic binder and as a filler at least ground and/or broken-up radioactive and/or toxic material with a fine component < 250 μm grain size of the filler being less than 30 wt.% based on the weight of the amount of filler.

31. Casting compound according to claim 30, wherein the at least one hydraulic binder is cement.

32. Casting compound according to claim 30, wherein the at least one radioactive and/or toxic material includes radioactive reactor graphite.

33. Casting compound according to claim 32, wherein the fine component < 250 μm grain size is less than 10 wt.% based on the weight of the amount of filler.

34. Casting containing radioactive materials to be disposed of as well as a casting or mortar recipe as a casting mortar matrix containing hydraulic binder and ground and/or broken-up radioactive graphite.

35. Casting according to claim 34, wherein the radioactive graphite of the mortar matrix includes reactor graphite.

36. Casting according to claim 34, wherein the radioactive materials to be disposed of include reactor waste.

37. Casting according to claim 34, wherein the hydraulic binder includes cement.

38. Casting material cast in a vessel as a mold, wherein the casting material comprises a casting mortar matrix containing hydraulic binder and

ground and/or broken-up radioactive graphite nearly devoid of ultrafine components.

39. Casting compound containing as a mortar or casting matrix a mortar or casting material recipe containing at least one hydraulic binder or ground and/or crushed reactor graphite as the filler made by the method according to claim 22.

<u>**REMARKS**</u>

Due to the number and nature of the corrections thereto, Applicants submit herewith a Substitute Specification, along with a marked-up copy of the Substitute Specification showing the changes therein made by amendment to the original specification. No new matter has been added to the original specification. The substitute specification includes the changes as shown in the marked-up copy and includes the newly added Brief Description of the Drawings and appropriate headings in the specification. Therefore, entry of the Substitute Specification is respectfully requested. Claims 1-16 have been canceled and new claims 17-39 have been added. Thus, claim 17-39 are in the application. An Information Disclosure Statement is filed herewith under separate cover letter.

An early action on the merits of the application is requested.

To the extent necessary, applicants petition for an extension of time under 37 CFR §1.136. Please charge any shortage in the fees due in connection with the filing of this paper, including extension of time fees, to Deposit Account

No. 01-2135 (635.40828X00) and please credit any excess fees to such deposit account.

Respectfully submitted,

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10/018091
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Disposal of Radioactive Materials

The present invention relates to a method for disposing of radioactive materials, especially radioactive graphite as an embedded material or a casting, especially made using the method defined above.

Disposal of radioactive waste, especially radioactive reactor graphite, is a problem that has not yet been solved. At the present time, radioactive and/or heavy toxic materials have been disposed of for so-called final storage using so-called compact conditioning or by solidification (embedding in cement, etc.), but this produces very large volumes of material that needs to be disposed of or stored. For example, no large quantities of reactor graphite have been disposed of yet in the United States, Great Britain, France, and Germany since there are no specific conditioning and disposal strategies there. In France and Great Britain, graphite combustion has been discussed as a possible approach, but such waste products must not be burned due to the large amounts of radioactive tritium (T) and carbon-14 (C-14) because this would bring about a considerable ecological burden as a result of emissions into the atmosphere. Especially in the United States and other countries, there is considerable objection to combustion. Disposal scenarios proposed according to the prior art, especially for disposal of radioactive graphite, are mentioned in the list of references attached hereto.

In addition, a method is proposed in US Patent 4,652,404 for conditioning radioactively contaminated waste by combustion followed by disposal of the resulting ashes by deposition in a bed of cement or concrete. Similarly, encapsulation of dangerous waste products is proposed in WO 98,54107, such as heavy metals, arsenic, etc. as well as radioactive materials. Encapsulation takes place in a curable system containing calcium carbonate and magnesium oxide.

DE 31 31 798 describes the mechanical breakup of fuel elements using a high-pressure stream of water. Following classification of the broken-up material, the graphite sludge eventually obtained is solidified with cement to produce blocks for final disposal.

Generally speaking, the prior art teaches the possibility of mixing graphite dry, with sand and cement for example, and then solidifying it by adding water to make blocks. However, it has turned out that the graphite/sand cement blocks thus produced have a poor compressive strength so that the disposal of radioactive graphite proposed in the prior art, for example by embedding in concrete, is not being continued at the present time.

Therefore, one of the goals of the present invention is to propose a disposal method improved over the methods known today, especially for getting rid of radioactive waste products such as radioactive graphite since, in the near future, there will be large amounts of waste, especially of radioactive reactor graphite waste.

According to the invention, this goal is achieved by means of a method according to the language of Claim 1.

The idea of the invention is that the radioactive waste that is to be disposed of, particularly the radioactive reactor graphite that is to be disposed of, after being ground or crushed, replaces aggregates and additives in appropriate binder or aggregate formulations for producing casting or embedding mortars for waste conditioning. It is essential to the invention that the proportion of fines in the material to be disposed of, for example, in the graphite, is small, i.e., that the proportion having an average grain size of < 250 µm amounts to less than 30 wt.%. Surprisingly, it has been shown that when the proportion of fines is reduced, the compressive strength of cement-bonded materials, which are produced for the disposal of radioactive wastes, could be considerably improved, most likely since too great a proportion of fines produces a certain lubricating effect, which leads to unacceptable, low compressive strengths.

Preferably, the fine components < 200 µm of the radioactive waste to be disposed of, especially the radioactive graphite to be disposed of, constitute less than 20% and even more preferably less than 15 wt.%.

According to one variant embodiment of the present invention, a formulation of sealing compound or casting mortar, which contains a hydraulic binder, such as, for example, cement mortar of commonly used sand or gravel, will be replaced by the ground or broken-up radioactive

material that is to be disposed of, particularly by the radioactive reactor graphite for disposal. Preferred variants of embodiment of the method according to the invention are characterized in the dependent claims.

The disposal of radioactive reactor graphite is thus accomplished by grinding wet, followed by complete substitution of additives such as sand and/or gravel and/or additives in the cement-bound material such as cement mortar and concrete, which are used for example in the form of a graphite/cement mortar matrix for filling otherwise waste-laden containers, such as containers and the like. As a result of this conditioning of the waste material, complete elimination of the otherwise resulting volume of waste created when radioactive reactor graphite is solidified, which would then be present alone or with other radioactive waste products as a finally conditioned drum of waste, is achieved. This method of graphite disposal is associated with considerable savings of expense from the financial standpoint, since otherwise high disposal costs would result from additional drums to be generated followed by storage.

Casting and filling mortars consisting of sand, cement binder, and special additives are frequently used for solidifying radioactive waste, as for example reactor shields, graphite segments, concrete fragments, etc., in which the mortar fills the spaces in the waste-laden containers and so forms a solid, monolithic waste drum unit. In contrast to this casting known from the prior art, the procedure proposed according to the invention has the advantage that the mortar to be loaded contained in the

spaces also contains radioactive materials, such as the above-mentioned radioactive reactor graphite.

The method of graphite disposal consists for example of the following steps:

- Wet grinding of radioactive reactor graphite by means of a grinder with a breaking mill known from stone chip production to produce grain sizes from 0 to approx. 60 mm diameter for substitution of aggregates and/or other additives such as up to 100% sand (here the grain size is up to 6 mm) as an aggregate in the cement-bonded recipe, which is about 45 wt.% in the filling mortar, containing cement which can be contained for final conditioning for solidification of other waste products to be disposed of in the containers. The addition of ground graphite can also take place beyond the amount of sand, by further substitution of additives up to 50 wt.% in the cement mortar.

Aggregate such as gravel and sand and other additives produced by broken-up and ground radioactive graphite can be substituted in the concrete material so that such concrete mixtures can contain up to 75 wt.% graphite.

Preferably, a graphite/cement ratio of at least 1.3 is chosen, and even more preferred a graphite/cement ratio of at least 1.35.

- Mixing the wet-ground graphite with a solidification matrix prepared for the purpose, e.g. cement-bonded material such as cement mortar, concrete, etc.

- Loading the radioactive, flowable reactor graphite-filling matrix that solidifies or bonds later in the preconditioned waste containers already loaded with other solid waste products to produce waste drums.

The method described by way of example for disposing of reactor graphite in the solidified filling matrix, which is used for example for making waste drums containing already preconditioned radioactive wastes, is shown in greater detail in Figures 1 and 2 by way of example. Solidification of weakly radioactive wet ground graphite to produce so-called "lost shields," in other words for shields for use in nuclear power plants as well as intermediate or final storage, is also possible.

Relative to the two Figures 1 and 2 mentioned above, Figure 1 shows in section an example of a container 1 containing various radioactive materials to be disposed of, which are enclosed in a casting matrix proposed according to the invention. Thus, Figure 1 shows schematically for example a graphite segment 3, graphite fragments 5, segments of a thermal or biological shield 7, as well as colemanite concrete fragments 9. These materials to be disposed of and cast in container 1 are embedded in a radioactive cement mortar matrix 11 containing graphite, proposed according to the invention.

Figure 2 shows in cross section another container drum 21, which can be for example a thin-walled small container made of concrete weighing about 20 tons, mainly containing

radioactive steel and gray cast iron waste, which had been used for example as shields in nuclear reactors.

The invention will now be explained in greater detail with reference to formulations provided as examples. The following Table 1 shows four recipes with maximum grain sizes of the graphite of 6 mm, 15 mm, 30 mm, and 60 mm.

Table 1

Maximum grain size of graphite	mm	6	15	30	60
Percentage < 200 µm	%	< 15	< 10	< 8	< 5
Graphite load dry	kg/m^3	809.0	1024.8	1189.7	1350.7
Graphite (2.5% H_2O)	g	310.0	490.4	692.4	980.8
Pore filler	g	55.0	56.1	56.7	57.0
Zeolite	g	29.7	30.3	30.6	30.8
Cement	g	184.0	187.7	189.6	190.7
Plasticizing medium	g	4.0	4.1	4.1	4.1
Wetting medium	g	0.6	0.6	0.6	0.6
Additive fraction	g	122.7	127.9	132.0	135.7
Σ Weighed amount without additive	g	583.3	769.2	974.0	1264.0
Surface of the graphite	cm^2	214811	216390	217198	217769
Raw density ρ_0 measured	g/cm^3	1.89	1.92	1.95	1.98
* Theoretically without air	g/cm^3	1.93	1.96	1.99	2.01
Air pores calculated	Vol.%	2.3	2.1	2.0	1.8
Compressive strength β_0 90 (average of 3 measurements)	N/mm^2	40.0 ± 5.0	40.0 ± 5.0	40.0 ± 5.0	40.0 ± 5.0
Graphite/cement ratio	C/Z	1.37-1.64	2.13-2.55	3.0-3.6	4.1-5.0

[1)]Reactor graphite with raw density dry = 1.70 kg/dm^3, wet = 1.87 kg/dm^3, and porosity = 17.34 vol.%.

The pore filler is an amorphous disperse silica, a binder for excess calcium hydroxide ($Ca(OH)_2$). The disperse silica serves to increase resistance to leaching.

Zeolite is a replacement agent for binding cesium and strontium, which are mobile radioactive fission products, which are usually easily soluble. The leaching of mobile radionuclides is impeded by the zeolite.

Possibly, the additives such as pore fillers and zeolite can be replaced by finely-ground graphite waste.

Portland cement or high-grade cement such as sulfate-resistant cement or corrosion-resistant cement, which are used especially in bridge-building and for applications under water, are advantageously used as the cement. Fundamentally, the following binders are possible:

Hydraulically-acting Portland cement, vertical kiln cement, fly ash cement, shale oil cement, aluminous cement, Ferrari cement, and white cement, alone, in combination, with one another, or with silica dust, pozzolan, hydraulic lime, calcium hydroxide, calcium oxide, magnesium hydroxide, magnesium oxide, calcium sulfate hemihydrate, anhydrous calcium sulfate, as well as inorganic geopolymers. Using reactive resins is also possible, such as epoxy resins, silicone resins, polyurethane resins, etc., alone or in combination with the above-mentioned binders.

An additive for optimizing the flowability or filling properties of the mortar mixture is used as a plasticizer.

Wetting agent: serves to wet the graphite surface and for preventing air inclusions. The wetting agent must not form complexes and should break down rapidly in the cement medium.

Two years after solidification (storage), a wetting agent should for the most part no longer be detectable.

The attached Figures 3 to 6 show the corresponding screen analyses of the graphites used in the four formulations, with a maximum grain size of 6 mm in Figure 3, 15 mm in Figure 4, 30 mm in Figure 5, and 60 mm in Figure 6.

In the following Table 2, the grain size distributions in the different graphite aggregates, with the maximum grain diameters of 6, 15, 30, and 60 mm, are listed as shown in Figures 3 to 6.

Table 2

Screen mesh Diameter	Passage through the screen			
[mm]	[wt.%]	[wt.%]	[wt.%]	[wt.]
60,000	–	–	–	100.0
30,000	–	–	100.0	70.6
15,000	–	100.0	70.8	50.0
6000	100.0	63.2	44.8	31.6
4000	81.2	51.3	36.3	25.7
2000	58.2	36.8	26.1	18.4
1000	39.2	24.8	17.6	12.4
0.500	27.7	17.5	12.4	8.8
0.250	19.4	12.2	8.7	6.1
0.125	12.5	7.9	5.6	3.9
0.00	0.0	0.0	0.0	0.0

As is clearly discernible from the four formulations, the recipe can include much less graphite when a maximum grain size of up to 60 mm is used, i.e. approx. 70% more than with a maximum grain size of the graphite of 6 mm. What formulation finally is used for casting further radioactive wastes, depends on the "bulkiness" or the dimensions of these waste products as well as the order of magnitude of the load of the graphite/cement mortar material. The greater the maximum grain size of the graphite in the mortar recipe, the higher is the graphite loading of the formulation.

A first investigation of compressive strength after a 28-day setting of samples produced from the four sample formulations of graphite/cement mortar mixtures yielded values of 42 N/mm^2 to 51 N/mm^2. The minimum compressive strength for solidified waste matrices of 10 N/mm^2, which is required by the HSK [Nuclear Plant Safety Department] and the NAGRA [National Society for the Disposal of Radioactive Waste], is thus clearly exceeded. The values measured generally meet the requirements of international standards relative to minimum compressive strength. The leaching data of radionuclides in demineralized and gypsum-saturated water (according to ISO Standard 6961) is $< 5 \times 10^{-6}$ m/d. Measurements of moldings produced with graphite with a substantially higher proportion of fines than that required according to the invention yield compressive strengths of less than 15 N/m^2. With graphite as the aggregate with a maximum grain size of 200 μm, compressive strengths of < 10 N/m^2 were measured.

The great advantage of the graphite/cement mortar formulations proposed according to the invention lies in the fact that, in addition to the embedding of any kind of radioactive wastes as well as liquids that must also be disposed of, radioactive reactor graphite can be disposed of instead of the commonly used sand or gravel or other additives. Thus a higher filling ratio than is common with the use of sand or of mineral fillers can be used.

References

1. M. Dubourg, Nuclear Engineering and Design 154 (175) Solution to level 3 dismantling of gas-cooled reactors: the graphite-incineration, pages 73-77.

2. Kontec '99, 4th International Symposium, "Conditioning of radioactive operating and shutdown wastes," March 15-17, 1999, St. Theis et al., Long-term guarantee values for C-14 on the example of the Morsleben final storage, pages 859-876.

3. V. Hesshaimer, M. Heimann, I. Levin, "Radiocarbon evidence for a smaller oceanic carbon dioxide sink than previously believed," Nature, Volume 370, No. 6485, July 21, 1994.

4. H. H. Lossli, Ingeborg Levin, Local and global ^{14}C concentrations and the radiation doses caused by them. Seminar on environmental pollution due to long-life radionuclides that are artificially produced, Lucerne and Vitznau, June 29 and 30, 1995.

Claims

1. Method for disposal of radioactive materials, characterized in that, in a binder/aggregate mixture for producing embedding materials, mortars, casting resins and the like, the aggregate is partially substituted by the material to be disposed of, and that the material to be disposed of is nearly devoid of ultrafine components.

2. Method, particularly according to Claim 1, characterized in that the proportion of fines of < 250 µm amounts to less than 30%, referred to the weight of the material to be disposed of, preferably less than 15 wt.%.

3. Method, particularly according to one of Claims 1 or 2, characterized in that a hydraulic binder is used as the binder, at least in part.

4. Method, particularly according to one of Claims 1 to 3, characterized in that a reaction resin is used as the binder, at least in part.

5. Method, particularly according to one of Claims 1 to 4, characterized in that the radioactive material is used as the aggregate and partially replaces filler with the binder as mortar or casting compound for embedding or encapsulating other materials to be disposed of in a receptacle or container.

6. Method, particularly according to one of Claims 1 to 5, characterized in that radioactive graphite, particularly

reactor graphite, is broken up into small pieces and is used at least with a preferably hydraulic binder, such as cement, as well as other additives as needed, as a mortar or casting compound formulation for embedding or encapsulating other radioactive and/or toxic materials, particularly reactor wastes or reactor parts to be disposed of.

7. Method, particularly according to one of Claims 1 to 6, characterized in that first radioactive reactor graphite is wet-ground to a grain size of < 60 mm, preferably < 30 mm and then is mixed together with at least one hydraulic binder such as cement for the production of a mortar or embedding compound formulation.

8. Method, particularly according to one of Claims 1 to 7, characterized in that the proportion of fines of < 200 μm of the material to be disposed of, particularly radioactive reactor graphite, amounts to less than 20%, referred to the weight of the material to be disposed of, preferably less than 15%, and still more preferably, less than 10 wt.%.

9. Method, particularly according to one of Claims 6 to 8, characterized in that formulation additives for increasing the flowability, filling ratio, corrosion resistance, resistance to aging, resistance to leaching, as well as for surface wettability are added.

10. Method, particularly according to one of Claims 6 to 9, characterized in that the filling ratio of the formulation with ground and/or broken-up radioactive graphite is higher

than the filling ratio when conventional mineralized fillers are used, particularly aggregates such as sand, gravel and/or additives such as clinoptilolith, micropoz, powdered limestone, quartz powder, and others.

11. Method, particularly according to one of Claims 1 to 10, characterized in that sulfate-resistant and/or corrosion-resistant cement is used as the binder.

12. Method, particularly according to one of Claims 6 to 11, characterized in that the material to be disposed of or the radioactive graphite has a wetting agent added to it, while it is being crushed or ground.

13. Casting compound (11) containing as the binder recipe at least one hydraulic binder, such as cement for example, and as the filler at least ground and or broken-up radioactive and/or toxic material such as radioactive reactor graphite with the fine component < 250 μm of the filler, particularly the radioactive reactor graphite, being less than 30 wt.% based on the weight of the amount of filler, preferably less than 15 wt.%, and even more preferably less than 10 wt.%.

14. Casting containing radioactive materials to be disposed of, especially reactor waste (3, 5, 7, 9) as well as a casting or mortar recipe as a casting mortar matrix (11) containing hydraulic binder, such as cement as well as ground and/or broken-up radioactive graphite, especially reactor graphite.

15. Casting material, particularly according to Claims 13 or 14, cast in a vessel as a mold, such as a container (1, 21) for example.

16. Casting compound containing as the mortar or casting matrix (11) a mortar or casting material recipe containing at least one hydraulic binder such as cement or ground and/or crushed reactor graphite as the filler made by a method, especially according to one of Claims 5 to 11.

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Substitute Specification

DISPOSAL OF RADIOACTIVE MATERIALS

Related Applications

This application is a Section 371 filing of International Application PCT/CH00/00268, filed May 16, 2000, the priority of which is claimed under 35 U.S.C. §120. The International Application claims priority of Switzerland Application No. 1108/99, filed June 14, 1999, the priority of which is claimed under 35 U.S.C. §119.

Field

The present invention relates to a method for disposing of radioactive materials, especially radioactive graphite as an embedded material or a casting, especially made using the method defined above.

Background

Disposal of radioactive waste, especially radioactive reactor graphite, is a problem that has not yet been solved. At the present time, radioactive and/or heavy toxic materials have been disposed of for so-called final storage using so-called compact conditioning or by solidification (embedding in cement, etc.), but this produces very large volumes of material that need to be disposed of or

stored. For example, no large quantities of reactor graphite have been disposed of yet in the United States, Great Britain, France, and Germany since there are no specific conditioning and disposal strategies there. In France and Great Britain, graphite combustion has been discussed as a possible approach, but such waste products must not be burned due to the large amounts of radioactive tritium (T) and carbon-14 (C-14) because this would bring about a considerable ecological burden as a result of emissions into the atmosphere. Especially in the United States and other countries, there is considerable objection to combustion. Disposal scenarios proposed according to the prior art, especially for disposal of radioactive graphite, are mentioned in the list of references attached hereto.

In addition, a method is proposed in US Patent 4,652,404 for conditioning radioactively contaminated waste by combustion followed by disposal of the resulting ashes by deposition in a bed of cement or concrete. Similarly, encapsulation of dangerous waste products is proposed in WO 98,54107, such as heavy metals, arsenic, etc. as well as radioactive materials. Encapsulation takes place in a curable system containing calcium carbonate and magnesium oxide.

DE 31 31 798 describes the mechanical breakup of fuel elements using a high-pressure stream of water. Following classification of the broken-up material, the graphite sludge eventually obtained is solidified with cement to produce blocks for final disposal.

Generally speaking, the prior art teaches the possibility of mixing graphite dry, with sand and cement for example, and then solidifying it by adding water to make blocks. However, it has turned out that the graphite/sand cement blocks thus produced have a poor compressive strength so that the disposal of radioactive graphite proposed in the prior art, for example by embedding in concrete, is not being continued at the present time.

Summary

Therefore, one of the goals of the present invention is to propose a disposal method improved over the methods known today, especially for getting rid of radioactive waste products such as radioactive graphite since, in the near future, there will be large amounts of waste, especially of radioactive reactor graphite waste.

According to the invention, this goal is achieved by means of a method for disposal of radioactive materials, comprising providing a binder/aggregate mixture for producing at least one of an embedding material, a mortar and a casting resin, wherein the aggregate is partially substituted by at least one radioactive material to be disposed of, and wherein the at least one radioactive material to be disposed of is nearly devoid of ultrafine components.

The idea of the invention is that the radioactive waste that is to be disposed of, particularly the radioactive reactor graphite that is to be disposed of, after being ground or crushed, replaces aggregates and additives in

appropriate binder or aggregate formulations for producing casting or embedding mortars for waste conditioning. It is essential to the invention that the proportion of fines in the material to be disposed of, for example, in the graphite, is small, i.e., that the proportion having an average grain size of < 250 pm amounts to less than 30 wt.%. Surprisingly, it has been shown that when the proportion of fines is reduced, the compressive strength of cement-bonded materials, which are produced for the disposal of radioactive wastes, could be considerably improved, most likely since too great a proportion of fines produces a certain lubricating effect, which leads to unacceptable, low compressive strengths.

Preferably, the fine components < 200 μm of the radioactive waste to be disposed of, especially the radioactive graphite to be disposed of, constitute less than 20% and even more preferably less than 15 wt.%.

According to one variant embodiment of the present invention, a formulation of sealing compound or casting mortar, which contains a hydraulic binder, such as, for example, cement mortar of commonly used sand or gravel, will be replaced by the ground or broken-up radioactive material that is to be disposed of, particularly by the radioactive reactor graphite for disposal. Preferred variants of embodiment of the method according to the invention are characterized in the dependent claims.

The disposal of radioactive reactor graphite is thus accomplished by grinding wet, followed by complete substitution of additives such as sand and/or

gravel and/or additives in the cement-'bound material such as cement mortar and concrete, which are used for example in the form of a graphite/cement mortar matrix for filling otherwise waste-laden containers, such as containers and the like. As a result of this conditioning of the waste material, complete elimination of the otherwise resulting volume of waste created when radioactive reactor graphite is solidified, which would then be present alone or with other radioactive waste products as a finally conditioned drum of waste, is achieved. This method of graphite disposal is associated with considerable savings of expense from the financial standpoint, since otherwise high disposal costs would result from additional drums to be generated followed by storage.

Casting and filling mortars consisting of sand, cement binder, and special additives are frequently used for solidifying radioactive waste, as for example reactor shields, graphite segments, concrete fragments, etc., in which the mortar fills the spaces in the waste-laden containers and so forms a solid, monolithic waste drum unit. In contrast to this casting known from the prior art, the procedure proposed according to the invention has the advantage that the mortar to be loaded contained in the spaces also contains radioactive materials, such as the above-mentioned radioactive reactor graphite.

The method of graphite disposal consists for example of the following steps:

- Wet grinding of radioactive reactor graphite by means of a grinder with a breaking mill known from stone chip production to produce grain sizes from

0 to approx. 60 mm diameter for substitution of aggregates and/or other additives such as up to 100% sand (here the grain size is up to 6 mm) as an aggregate in the cement-bonded recipe, which is about 45 wt.% in the filling mortar, containing cement which can be contained for final conditioning for solidification of other waste products to be disposed of in the containers. The addition of ground graphite can also take place beyond the amount of sand, by further substitution of additives up to 50 wt.% in the cement mortar.

Aggregate such as gravel and sand and other additives produced by broken-up and ground radioactive graphite can be substituted in the concrete material so that such concrete mixtures can contain up to 75 wt,% graphite.

Preferably, a graphite/cement ratio of at least 1.3 is chosen, and even more preferred a graphite/cement ratio of at least 1.35.

- Mixing the wet-ground graphite with a solidification matrix prepared for the purpose, e.g. cement-bonded material such as cement mortar, concrete, etc.
- Loading the radioactive, flowable reactor graphite-filling matrix that solidifies or bonds later in the preconditioned waste containers already loaded with other solid waste products to produce waste drums.

<u>Brief Description of the Drawings</u>

Fig. 1 shows in section an example of a container of the present invention containing various radioactive materials to be disposed of.

Fig. 2 shows in cross-section another container drum made of concrete

weighing about 20 tons, containing radioactive steel and gray cast iron waste, which has been used for example as shields in nuclear reactors.

Fig. 3 shows a screen analysis of the graphite used in one formulation of the invention, with a maximum grain size of 6 mm.

Fig. 4 shows a screen analysis of a graphite used in a second formulation of the invention, with a maximum grain size of 15 mm.

Fig. 5 shows a screen analysis of a graphite used, in a third formulation of the invention, with a maximum grain size of 30 mm.

Fig. 6 presents a screen analysis of a graphite used in a fourth formulation of the invention, with a maximum grain size of 60 mm.

Detailed Description

The method described by way of example for disposing of reactor graphite in the solidified filling matrix, which is used for example for making waste drums containing already preconditioned radioactive wastes, is shown in greater detail in Figures 1 and 2 by way of example. Solidification of weakly radioactive wet ground graphite to produce so-called “lost shields,” in other words for shields for use in nuclear power plants as well as intermediate or final storage, is also possible.

Relative to the two Figures 1 and 2 mentioned above, Figure 1 shows in section an example of a container 1 containing various radioactive materials to be disposed of, which are enclosed in a casting matrix proposed according to the

invention. Thus, Figure 1 shows schematically for example a graphite segment 3, graphite fragments 5, segments of a thermal or biological shield 7, as well as colemanite concrete fragments 9. These materials to be disposed of and cast in container 1 are embedded in a radioactive cement mortar matrix 11 containing graphite, proposed according to the invention.

Figure 2 shows in cross section another container drum 21, which can be for example a thin-walled small container made of concrete weighing about 20 tons, mainly containing radioactive steel and gray cast iron waste, which had been used for example as shields in nuclear reactors.

The invention will now be explained in greater detail with reference to formulations provided as examples. The following Table 1 shows four recipes with maximum grain sizes of the graphite of 6 mm, 15 mm, 30 mm, and 60 mm.

Table 1

Maximum grain size of graphite	mm	6	15	30	60
Percentage < 200 µm	%	< 15	< 10	< 8	< 5
Graphite load dry	kg/m^3	809.0	1024.8	1189.7	1350.7
Graphite (2.5% H_20)	g	310.0	490.4	692.4	980.8
Pore filler	g	55.0	56.1	56.7	57.0
Zeolite		29.7	30.3	30.6	30.8
Cement	g	184.0	187.7	189.6	190.7
Plasticizing medium	g	4.0	4.1	4.1	4.1
Wetting medium	g	0.6	0.6	0.6	0.6
Additive fraction	g	122.7	127.9	132.0	135.7
Σ Weighed amount without additive	g	583.3	769.2	974.0	1264.0
Surface of the graphite	cm^2	214811	216390	217198	217769
Raw density ρ_0 measured	g/cm^3	1.89	1.92	1.95	1.98
* Theoretically without air	g/cm^3	1.93	1.96	1.99	2.01
Air pores calculated	Vol.%	2.3	2.1	2.0	1.8
Compressive strength β_0 90 (average of 3 measurements)	N/mm^2	40.0 ± 5.0	40.0 ± 5.0	40.0 ± 5.0	40.0 ± 5.0
Graphite/cement ratio	C/Z	1.37—1.64	2.13—2.55	3.0—3.6	4.1—5.0

[1)]Reactor graphite with raw density dry = 1.70 kg/dm^3, wet = 1.87 kg/dm^3, and porosity = 17.34 vol.%.

The pore filler is an amorphous disperse silica, a binder for excess calcium hydroxide ($Ca(OH)_2$). The disperse silica serves to increase resistance to leaching.

Zeolite is a replacement agent for binding cesium and strontium, which are mobile radioactive fission products, which are usually easily soluble. The leaching of mobile radionuclides is impeded by the zeolite.

Possibly, the additives such as pore fillers and zeolite can be replaced by finely-ground graphite waste.

Portland cement or high-grade cement such as sulfate-resistant cement or corrosion-resistant cement, which are used especially in bridge-building and for applications under water, are advantageously used as the cement. Fundamentally, the following binders are possible:

Hydraulically-acting Portland cement, vertical kiln cement, fly ash cement, shale oil cement, aluminous cement, Ferrari cement, and white cement, alone, in combination, with one another, or with silica dust, pozzolan, hydraulic lime, calcium hydroxide, calcium oxide, magnesium hydroxide, magnesium oxide, calcium sulfate hemihydrate, anhydrous calcium sulfate, as well as inorganic geopolymers. Using reactive resins is also possible, such as epoxy resins, silicone resins, polyurethane resins, etc., alone or in combination with the above-mentioned binders.

An additive for optimizing the flowability or filling properties of the

mortar mixture is used as a plasticizer.

Wetting agent: serves to wet the graphite surface and for preventing air inclusions. The wetting agent must not form complexes and should break down rapidly in the cement medium.

Two years after solidification (storage), a wetting agent should for the most part no longer be detectable.

The attached Figures 3 to 6 show the corresponding screen analyses of the graphites used in the four formulations, with a maximum grain size of 6 mm in Figure 3, 15 mm in Figure 4, 30 mm in Figure 5, and 60 mm in Figure 6.

In the following Table 2, the grain size distributions in the different graphite aggregates, with the maximum grain diameters of 6, 15, 30, and 60 mm, are listed as shown in Figures 3 to 6.

Table 2

Screen mesh Diameter			Passage through the screen	
[mm]	[wt.%]	[wt.%]	[wt.%]	[wt.]
60,000	0	0	0	100.0
30,000	0	0	100.0	70.6
15,000	0	100.0	70.8	50.0
6000	100.0	63.2	44.8	31.6
4000	81.2	51.3	36.3	25.7
2000	58.2	36.8	26.1	18.4
1000	39.2	24.8	17.6	12.4
0.500	27.7	17.5	12.4	8.8
0.250	19.4	12.2	8.7	6.1
0.125	12.5	7.9	5.6	3.9
0.00	0.0	0.0	0.0	0.0

As is clearly discernible from the four formulations, the recipe can include much less graphite when a maximum grain size of up to 60 mm is used, i.e., approx. 70% more than with a maximum grain size of the graphite of 6 mm. What formulation finally is used for casting further radioactive waste, depends on the "bulkiness" or the dimensions of these waste products a well as the order of magnitude of load of the graphite/cement mortar material. The greater the maximum grain size of the graphite in the mortar recipe, the higher is the graphite loading of the formulation.

A first investigation of compressive strength after a 28-day setting of sample produced from the four sample formulations of graphite/cement mortar mixtures yielded values of 42 N/mm^2 to 51 N/mm^2. The minimum compressive strength for solidified waste matrices of 10 N/mm^2, which is required by the HSK [Nuclear Plant Safety Department/ and the NAGRA [National Society for the Disposal of Radioactive Waste], is thus clearly exceeded. The values measured generally meet the requirements of international standards relative to minimum compressive strength. The leaching data of radionuclides in demineralized and gypsum-saturated waste (according to ISO Standard 6961) is $< 5 \times 10^{-6}$ m/d. Measurements of moldings produced with graphite with a substantially higher proportion of fines than that required according to the invention yield compressive strengths of less than 15 N/m^2. With graphite as

the aggregate with a maximum grain size of 200 μm, compressive strengths of < 10 N/m^2 were measured.

The great advantage of the graphite/cement mortar formulations proposed according to the invention lies in the fact that, in addition to the embedding of any kind of radioactive wastes as well as liquids that must also be disposed of, radioactive reactor graphite can be disposed of instead of the commonly used sand or gravel or other additives. Thus a higher filling ratio than is common with the use of sand or of mineral fillers can be used.

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Marked-up copy of Substitute Specification showing changes from original specification

DISPOSAL OF RADIOACTIVE MATERIALS

Related Applications

This application is a Section 371 filing of International Application PCT/CH00/00268, filed May 16, 2000, the priority of which is claimed under 35 U.S.C. §120. The International Application claims priority of Switzerland Application No. 1108/99, filed June 14, 1999, the priority of which is claimed under 35 U.S.C. §119.

Field

The present invention relates to a method for disposing of radioactive materials, especially radioactive graphite as an embedded material or a casting, especially made using the method defined above.

Background

Disposal of radioactive waste, especially radioactive reactor graphite, is a problem that has not yet been solved. At the present time, radioactive and/or heavy toxic materials have been disposed of for so-called final storage using so-called compact conditioning or by solidification (embedding in cement, etc.), but this produces very large volumes of material that [needs] need to be disposed of or stored. For example, no large quantities of reactor graphite have

been disposed of yet in the United States, Great Britain, France, and Germany since there are no specific conditioning and disposal strategies there. In France and Great Britain, graphite combustion has been discussed as a possible approach, but such waste products must not be burned due to the large amounts of radioactive tritium (T) and carbon-14 (C-14) because this would bring about a considerable ecological burden as a result of emissions into the atmosphere. Especially in the United States and other countries, there is considerable objection to combustion. Disposal scenarios proposed according to the prior art, especially for disposal of radioactive graphite, are mentioned in the list of references attached hereto.

In addition, a method is proposed in US Patent 4,652,404 for conditioning radioactively contaminated waste by combustion followed by disposal of the resulting ashes by deposition in a bed of cement or concrete. Similarly, encapsulation of dangerous waste products is proposed in WO 98,54107, such as heavy metals, arsenic, etc. as well as radioactive materials. Encapsulation takes place in a curable system containing calcium carbonate and magnesium oxide.

DE 31 31 798 describes the mechanical breakup of fuel elements using a high-pressure stream of water. Following classification of the broken-up material, the graphite sludge eventually obtained is solidified with cement to produce blocks for final disposal.

Generally speaking, the prior art teaches the possibility of mixing graphite dry, with sand and cement for example, and then solidifying it by adding water to make blocks. However, it has turned out that the graphite/sand cement blocks thus produced have a poor compressive strength so that the disposal of radioactive graphite proposed in the prior art, for example by embedding in concrete, is not being continued at the present time.

Summary

Therefore, one of the goals of the present invention is to propose a disposal method improved over the methods known today, especially for getting rid of radioactive waste products such as radioactive graphite since, in the near future, there will be large amounts of waste, especially of radioactive reactor graphite waste.

According to the invention, this goal is achieved by means of a method [according to the language of Claim 1] for disposal of radioactive materials, comprising providing a binder/aggregate mixture for producing at least one of an embedding material, a mortar and a casting resin, wherein the aggregate is partially substituted by at least one radioactive material to be disposed of, and wherein the at least one radioactive material to be disposed of is nearly devoid of ultrafine components.

The idea of the invention is that the radioactive waste that is to be disposed of, particularly the radioactive reactor graphite that is to be disposed

of, after being ground or crushed, replaces aggregates and additives in appropriate binder or aggregate formulations for producing casting or embedding mortars for waste conditioning. It is essential to the invention that the proportion of fines in the material to be disposed of, for example, in the graphite, is small, i.e., that the proportion having an average grain size of < 250 pm amounts to less than 30 wt.%. Surprisingly, it has been shown that when the proportion of fines is reduced, the compressive strength of cement-bonded materials, which are produced for the disposal of radioactive wastes, could be considerably improved, most likely since too great a proportion of fines produces a certain lubricating effect, which leads to unacceptable, low compressive strengths.

Preferably, the fine components < 200 μm of the radioactive waste to be disposed of, especially the radioactive graphite to be disposed of, constitute less than 20% and even more preferably less than 15 wt.%.

According to one variant embodiment of the present invention, a formulation of sealing compound or casting mortar, which contains a hydraulic binder, such as, for example, cement mortar of commonly used sand or gravel, will be replaced by the ground or broken-up radioactive material that is to be disposed of, particularly by the radioactive reactor graphite for disposal. Preferred variants of embodiment of the method according to the invention are characterized in the dependent claims.

The disposal of radioactive reactor graphite is thus accomplished by grinding wet, followed by complete substitution of additives such as sand and/or gravel and/or additives in the cement-'bound material such as cement mortar and concrete, which are used for example in the form of a graphite/cement mortar matrix for filling otherwise waste-laden containers, such as containers and the like. As a result of this conditioning of the waste material, complete elimination of the otherwise resulting volume of waste created when radioactive reactor graphite is solidified, which would then be present alone or with other radioactive waste products as a finally conditioned drum of waste, is achieved. This method of graphite disposal is associated with considerable savings of expense from the financial standpoint, since otherwise high disposal costs would result from additional drums to be generated followed by storage.

Casting and filling mortars consisting of sand, cement binder, and special additives are frequently used for solidifying radioactive waste, as for example reactor shields, graphite segments, concrete fragments, etc., in which the mortar fills the spaces in the waste-laden containers and so forms a solid, monolithic waste drum unit. In contrast to this casting known from the prior art, the procedure proposed according to the invention has the advantage that the mortar to be loaded contained in the spaces also contains radioactive materials, such as the above-mentioned radioactive reactor graphite.

The method of graphite disposal consists for example of the following steps:

- Wet grinding of radioactive reactor graphite by means of a grinder with a breaking mill known from stone chip production to produce grain sizes from 0 to approx. 60 mm diameter for substitution of aggregates and/or other additives such as up to 100% sand (here the grain size is up to 6 mm) as an aggregate in the cement-bonded recipe, which is about 45 wt.% in the filling mortar, containing cement which can be contained for final conditioning for solidification of other waste products to be disposed of in the containers. The addition of ground graphite can also take place beyond the amount of sand, by further substitution of additives up to 50 wt.% in the cement mortar.

Aggregate such as gravel and sand and other additives produced by broken-up and ground radioactive graphite can be substituted in the concrete material so that such concrete mixtures can contain up to 75 wt,% graphite.

Preferably, a graphite/cement ratio of at least 1.3 is chosen, and even more preferred a graphite/cement ratio of at least 1.35.

- Mixing the wet-ground graphite with a solidification matrix prepared for the purpose, e.g. cement-bonded material such as cement mortar, concrete, etc.
- Loading the radioactive, flowable reactor graphite-filling matrix that solidifies or bonds later in the preconditioned waste containers already loaded with other solid waste products to produce waste drums.

Brief Description of the Drawings

Fig. 1 shows in section an example of a container of the present invention containing various radioactive materials to be disposed of.

Fig. 2 shows in cross-section another container drum made of concrete weighing about 20 tons, containing radioactive steel and gray cast iron waste, which has been used for example as shields in nuclear reactors.

Fig. 3 shows a screen analysis of the graphite used in one formulation of the invention, with a maximum grain size of 6 mm.

Fig. 4 shows a screen analysis of a graphite used in a second formulation of the invention, with a maximum grain size of 15 mm.

Fig. 5 shows a screen analysis of a graphite used, in a third formulation of the invention, with a maximum grain size of 30 mm.

Fig. 6 presents a screen analysis of a graphite used in a fourth formulation of the invention, with a maximum grain size of 60 mm.

Detailed Description

The method described by way of example for disposing of reactor graphite in the solidified filling matrix, which is used for example for making waste drums containing already preconditioned radioactive wastes, is shown in greater detail in Figures 1 and 2 by way of example. Solidification of weakly radioactive wet ground graphite to produce so-called "lost shields," in other

words for shields for use in nuclear power plants as well as intermediate or final storage, is also possible.

Relative to the two Figures 1 and 2 mentioned above, Figure 1 shows in section an example of a container 1 containing various radioactive materials to be disposed of, which are enclosed in a casting matrix proposed according to the invention. Thus, Figure 1 shows schematically for example a graphite segment 3, graphite fragments 5, segments of a thermal or biological shield 7, as well as colemanite concrete fragments 9. These materials to be disposed of and cast in container 1 are embedded in a radioactive cement mortar matrix 11 containing graphite, proposed according to the invention.

Figure 2 shows in cross section another container drum 21, which can be for example a thin-walled small container made of concrete weighing about 20 tons, mainly containing radioactive steel and gray cast iron waste, which had been used for example as shields in nuclear reactors.

The invention will now be explained in greater detail with reference to formulations provided as examples. The following Table 1 shows four recipes with maximum grain sizes of the graphite of 6 mm, 15 mm, 30 mm, and 60 mm.

Table 1

Maximum grain size of graphite	mm	6	15	30	60
Percentage < 200 µm	%	< 15	< 10	< 8	< 5
Graphite load dry	kg/m^3	809.0	1024.8	1189.7	1350.7
Graphite (2.5% H_2O)	g	310.0	490.4	692.4	980.8
Pore filler	g	55.0	56.1	56.7	57.0
Zeolite		29.7	30.3	30.6	30.8
Cement	g	184.0	187.7	189.6	190.7
Plasticizing medium	g	4.0	4.1	4.1	4.1
Wetting medium	g	0.6	0.6	0.6	0.6
Additive fraction	g	122.7	127.9	132.0	135.7
Σ Weighed amount without additive	g	583.3	769.2	974.0	1264.0
Surface of the graphite	cm^2	214811	216390	217198	217769
Raw density ρ_0 measured	g/cm^3	1.89	1.92	1.95	1.98
* Theoretically without air	g/cm^3	1.93	1.96	1.99	2.01
Air pores calculated	Vol.%	2.3	2.1	2.0	1.8
Compressive strength β_0 90 (average of 3 measurements)	N/mm^2	40.0 ± 5.0	40.0 ± 5.0	40.0 ± 5.0	40.0 ± 5.0
Graphite/cement ratio	C/Z	1.37—1.64	2.13—2.55	3.0—3.6	4.1—5.0

[1)]Reactor graphite with raw density dry = 1.70 kg/dm^3, wet = 1.87 kg/dm^3, and porosity = 17.34 vol.%.

The pore filler is an amorphous disperse silica, a binder for excess calcium hydroxide ($Ca(OH)_2$). The disperse silica serves to increase resistance to leaching.

Zeolite is a replacement agent for binding cesium and strontium, which are mobile radioactive fission products, which are usually easily soluble. The leaching of mobile radionuclides is impeded by the zeolite.

Possibly, the additives such as pore fillers and zeolite can be replaced by finely-ground graphite waste.

Portland cement or high-grade cement such as sulfate-resistant cement or corrosion-resistant cement, which are used especially in bridge-building and for applications under water, are advantageously used as the cement. Fundamentally, the following binders are possible:

Hydraulically-acting Portland cement, vertical kiln cement, fly ash cement, shale oil cement, aluminous cement, Ferrari cement, and white cement, alone, in combination, with one another, or with silica dust, pozzolan, hydraulic lime, calcium hydroxide, calcium oxide, magnesium hydroxide, magnesium oxide, calcium sulfate hemihydrate, anhydrous calcium sulfate, as well as inorganic geopolymers. Using reactive resins is also possible, such as epoxy resins, silicone resins, polyurethane resins, etc., alone or in combination with the above-mentioned binders.

An additive for optimizing the flowability or filling properties of the

mortar mixture is used as a plasticizer.

Wetting agent: serves to wet the graphite surface and for preventing air inclusions. The wetting agent must not form complexes and should break down rapidly in the cement medium.

Two years after solidification (storage), a wetting agent should for the most part no longer be detectable.

The attached Figures 3 to 6 show the corresponding screen analyses of the graphites used in the four formulations, with a maximum grain size of 6 mm in Figure 3, 15 mm in Figure 4, 30 mm in Figure 5, and 60 mm in Figure 6.

In the following Table 2, the grain size distributions in the different graphite aggregates, with the maximum grain diameters of 6, 15, 30, and 60 mm, are listed as shown in Figures 3 to 6.

Table 2

Screen mesh Diameter	Passage through the screen			
[mm]	[wt.%]	[wt.%]	[wt.%]	[wt.]
60,000	0	0	0	100.0
30,000	0	0	100.0	70.6
15,000	0	100.0	70.8	50.0
6000	100.0	63.2	44.8	31.6
4000	81.2	51.3	36.3	25.7
2000	58.2	36.8	26.1	18.4
1000	39.2	24.8	17.6	12.4
0.500	27.7	17.5	12.4	8.8
0.250	19.4	12.2	8.7	6.1
0.125	12.5	7.9	5.6	3.9
0.00	0.0	0.0	0.0	0.0

As is clearly discernible from the four formulations, the recipe can include much less graphite when a maximum grain size of up to 60 mm is used, i.e., approx. 70% more than with a maximum grain size of the graphite of 6 mm. What formulation finally is used for casting further radioactive waste, depends on the "bulkiness" or the dimensions of these waste products a well as the order of magnitude of load of the graphite/cement mortar material. The greater the maximum grain size of the graphite in the mortar recipe, the higher is the graphite loading of the formulation.

A first investigation of compressive strength after a 28-day setting of sample produced from the four sample formulations of graphite/cement mortar mixtures yielded values of 42 N/mm^2 to 51 N/mm^2. The minimum compressive strength for solidified waste matrices of 10 N/mm^2, which is required by the HSK [Nuclear Plant Safety Department/ and the NAGRA [National Society for the Disposal of Radioactive Waste], is thus clearly exceeded. The values measured generally meet the requirements of international standards relative to minimum compressive strength. The leaching data of radionuclides in demineralized and gypsum-saturated waste (according to ISO Standard 6961) is $< 5 \times 10^{-6}$ m/d. Measurements of moldings produced with graphite with a substantially higher proportion of fines than that required according to the invention yield compressive strengths of less than 15 N/m^2. With graphite as

the aggregate with a maximum grain size of 200 μm, compressive strengths of $< 10\ N/m^2$ were measured.

The great advantage of the graphite/cement mortar formulations proposed according to the invention lies in the fact that, in addition to the embedding of any kind of radioactive wastes as well as liquids that must also be disposed of, radioactive reactor graphite can be disposed of instead of the commonly used sand or gravel or other additives. Thus a higher filling ratio than is common with the use of sand or of mineral fillers can be used.

[Figure 3, left:]

Passage through the sieve (weight %)

[bottom:]

Mesh width (mm)

SIA-A, Grind 1

SIA-B, Grind 2

[Figure 4, left:]

Passage through a sieve (weight %)

[bottom:]

Mesh width (mm)

[Figure 5, left:]

Passage through a sieve (weight %)

[bottom:]

Mesh width (mm)

[Figure 6, left:]

Passage through a sieve (weight %)

[bottom]

Mesh width (mm)

ABSTRACT OF THE DISCLOSURE

A method for the disposal of radioactive materials, in which the loading material in a binding agent/loading material/additive mixture for the production of casting compound, mortar, casting resin and the like is at least partially substituted by the material to be eliminated. In the operation, it is essential for the fine fraction < 250 μm of the material to be eliminated to be less than 30% by weight in relation to the weight of the material to be eliminated, preferably less than 15% by weight. The binding agent/loading material/additive mixture can be used as mortar or casting compound for casting or encapsulating additional material to be eliminated in a receptacle or container. The binding agent/loading material/additive mixture is particularly suitable for the disposal of reactor graphite.

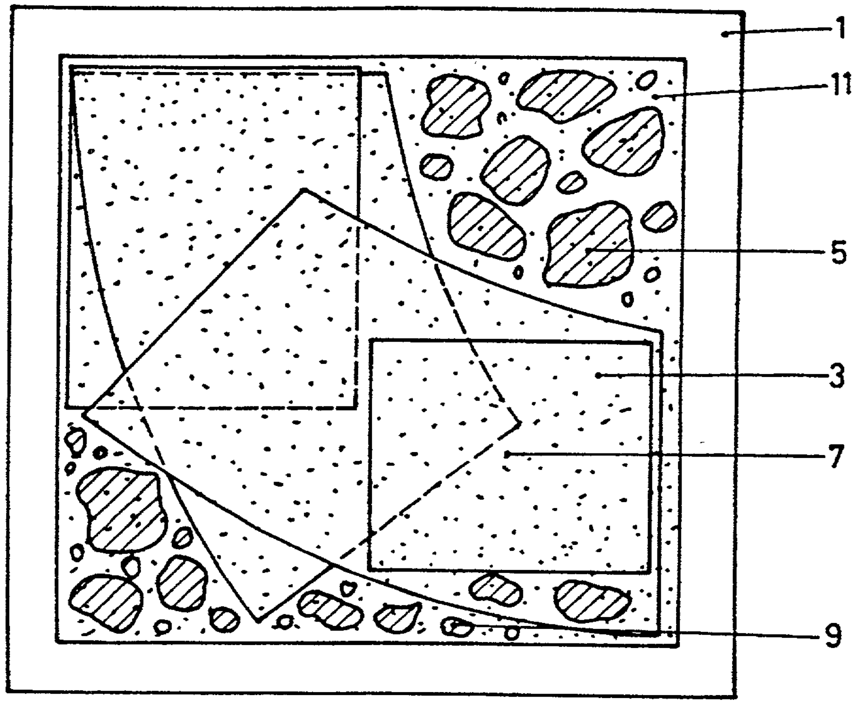

FIG.1

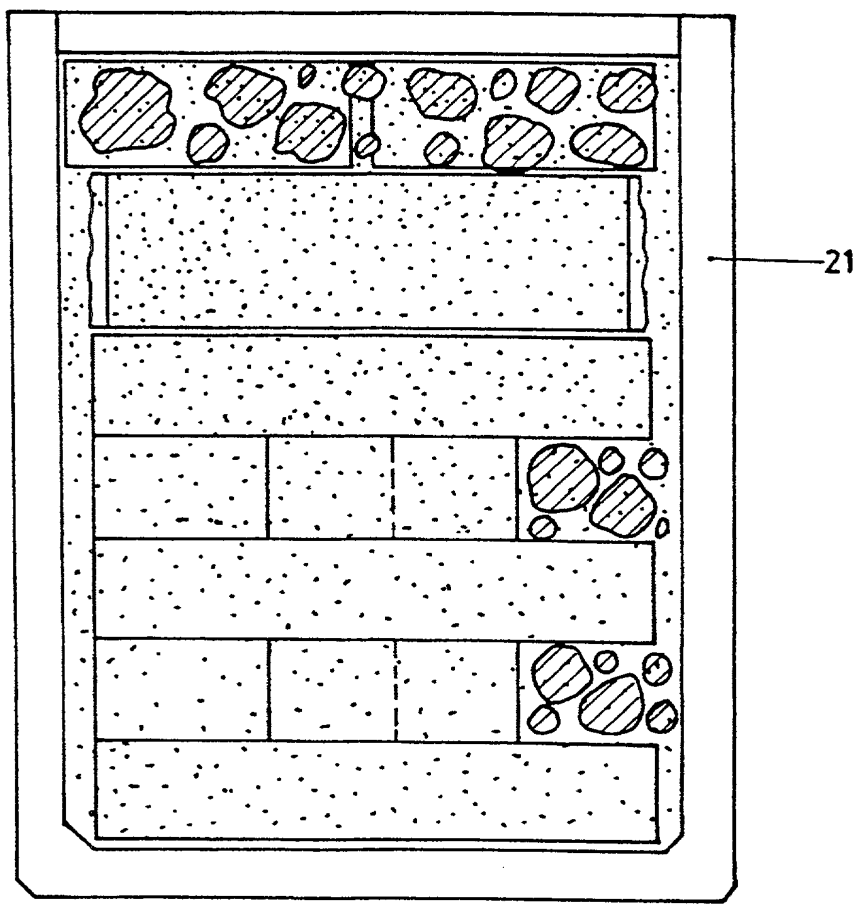

FIG.2

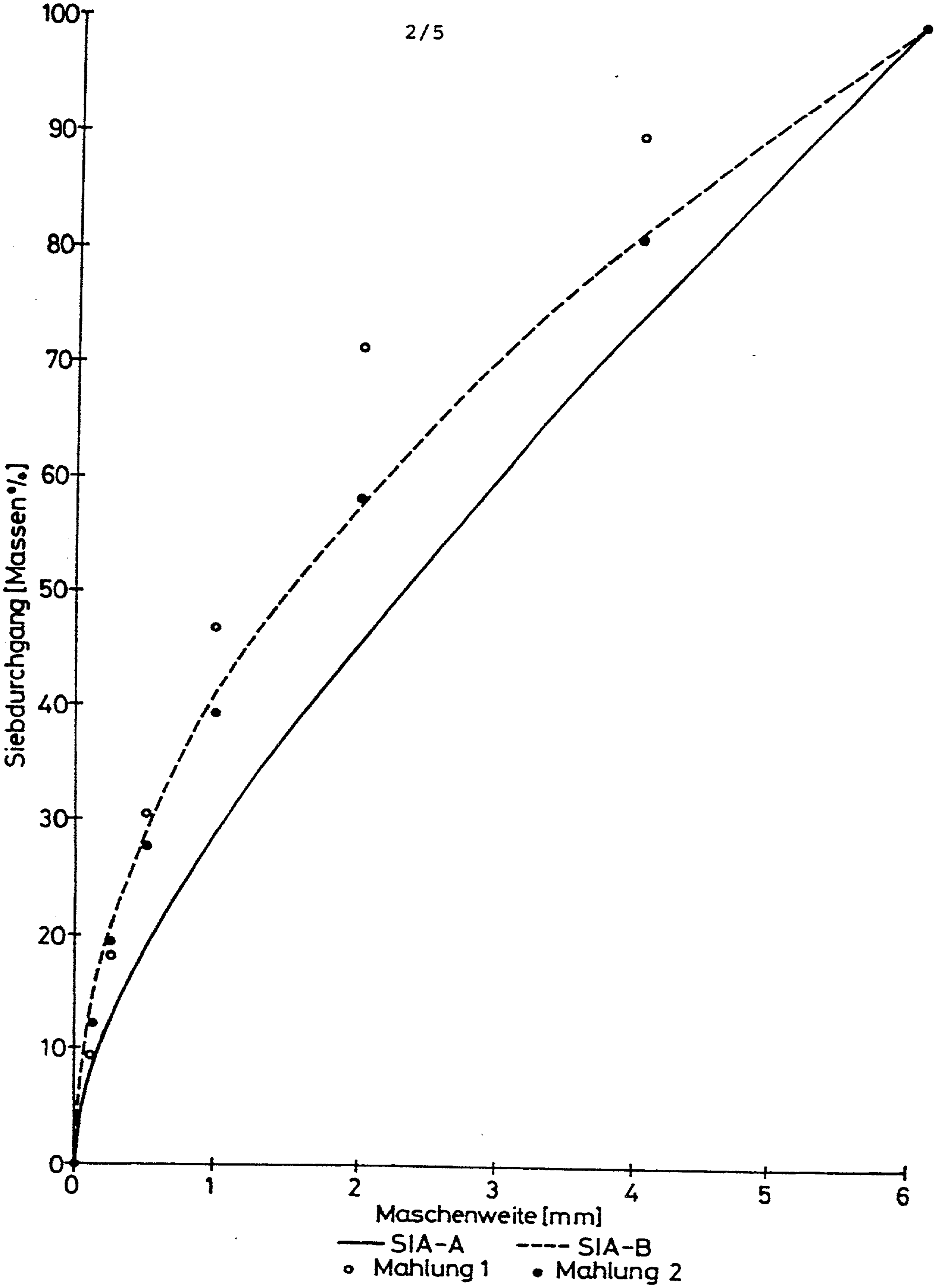
100
90
80
70
60
50
40
30
20
10
0
Siebdurchgang [Massen %]
0
1
2
3
4
5
6
Maschenweite [mm]
SIA-A
SIA-B
Mahlung 1
Mahlung 2

FIG.3

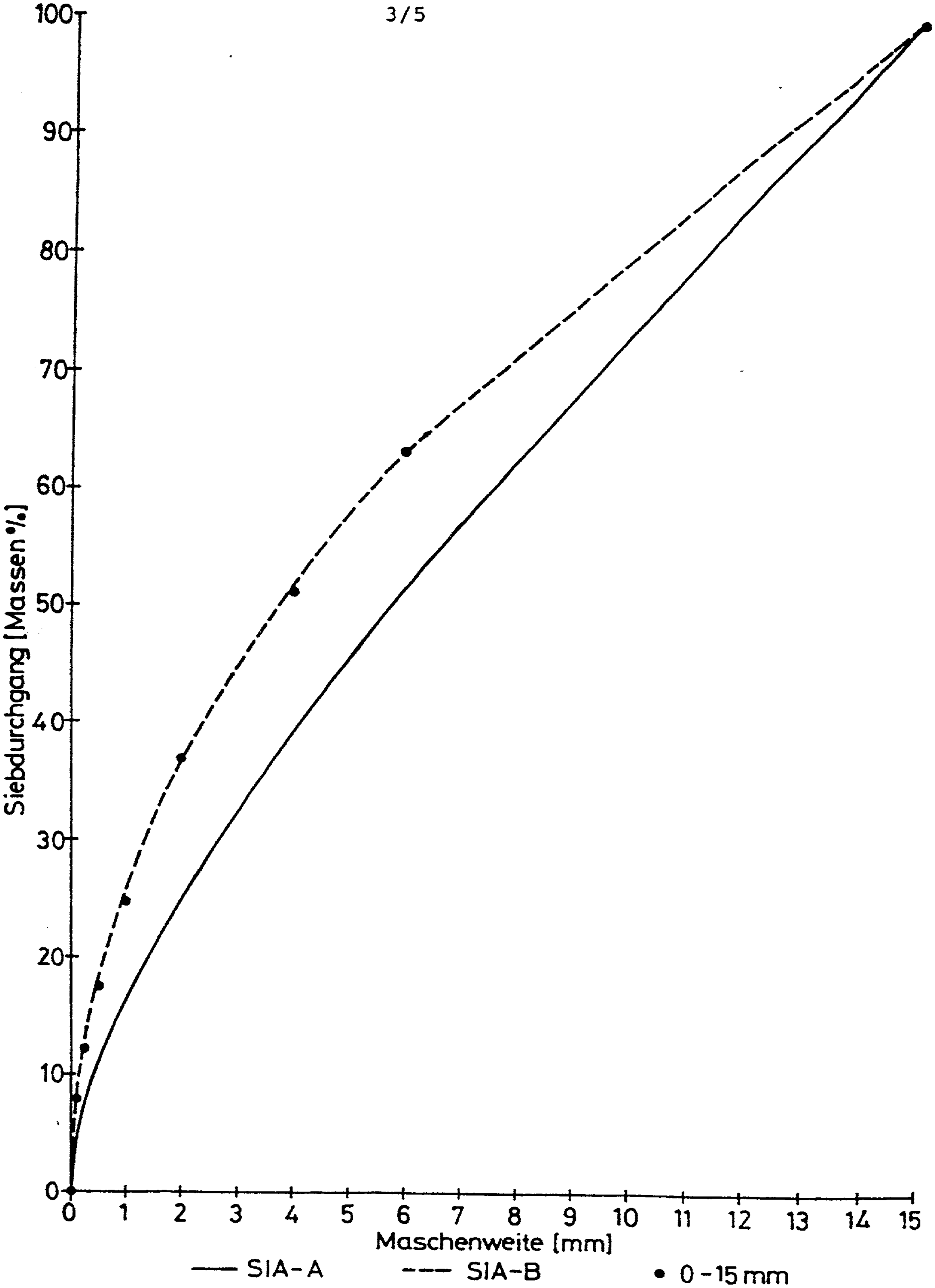
Siebdurchgang [Massen %]
0
10
20
30
40
50
60
70
80
90
100
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Maschenweite [mm]
SIA-A
SIA-B
0-15 mm

FIG. 4

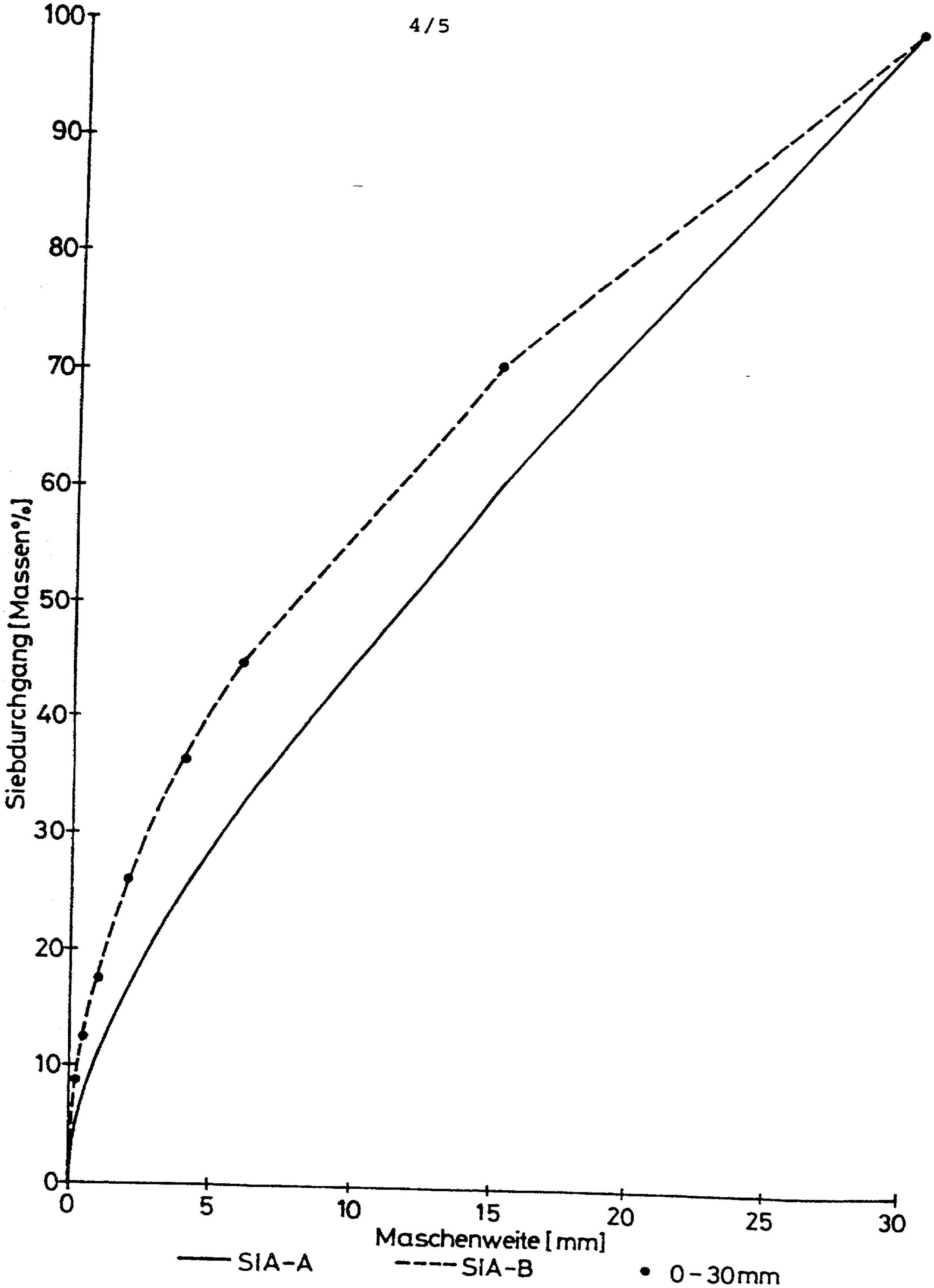
100
90
80
70
60
50
40
30
20
10
0
Siebdurchgang [Massen%]
0
5
10
15
20
25
30
Maschenweite [mm]
SIA-A
SIA-B
0-30mm

FIG.5

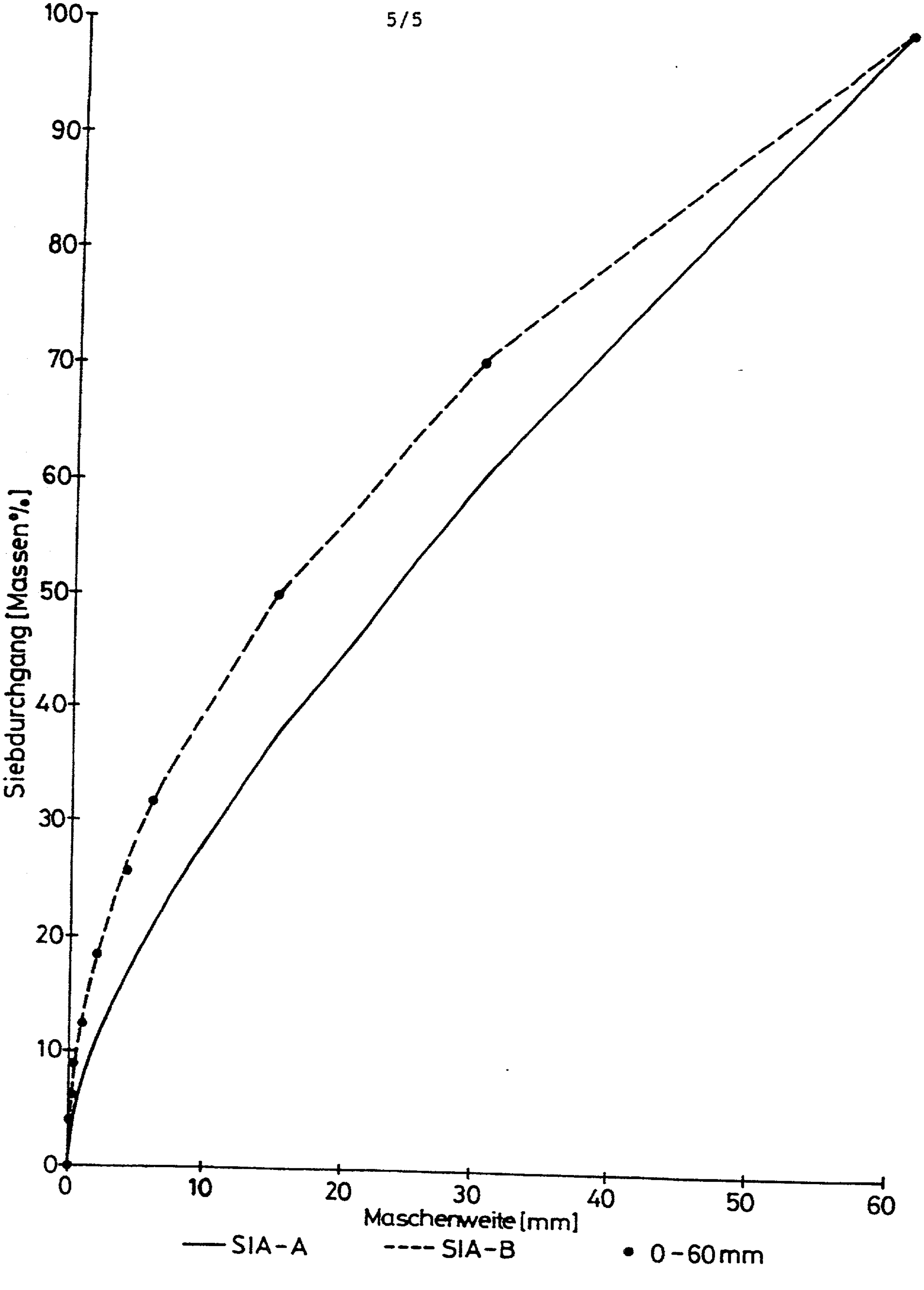
Siebdurchgang [Massen%]
0
10
20
30
40
50
60
70
80
90
100
Maschenweite [mm]
0
10
20
30
40
50
60
SIA-A
SIA-B
0-60mm

FIG.6

P201225

Attorney's Docket No.: 635.40828X00

DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

As a below named inventor, I hereby declare that: my residence, post office address and country of citizenship are as stated below, next to my name; I believe I am the original, first, and sole inventor (if only one name is listed below) or an original, first, and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

DISPOSAL OF RADIOACTIVE MATERIALS

the specification of which

___ is attached hereto.

x was filed on **December 14, 2001** as

United States Application Number **10/018,091**

or PCT International Application Number **PCT/CH00/00268**

and was amended on ________________.

(if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claim(s), as amended by any amendment referred to above. I acknowledge the duty to disclose all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d), of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

(Number)	(Country)	(Day/Month/Year Filed)	Priority Claimed Yes	No
1108/99	**Switzerland**	**14 June 1999**	X	
			X	

I hereby claim the benefit under title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below

(Application Number)	Filing Date

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Number)	Filing Date	(Status -- patented, pending, abandoned)
(Application Number)	Filing Date	(Status -- patented, pending, abandoned)

I hereby appoint: Donald R. Antonelli, Reg. No. 20,296; Melvin Kraus, Reg. No. 22,466; William I. Solomon, Reg. No. 28,565; Gregory E. Montone, Reg. No. 28,141; Ronald J. Shore, Reg. No. 28,577; Donald E. Stout, Reg. No. 26,422; Alan E. Schiavelli, Reg. No. 32,087; James N. Dresser, Reg. No. 22,973; Carl I. Brundidge, Reg. No. 29,621; Paul J. Skwierawski, Reg. No. 32,173; Robert M. Bauer, Reg. No. 34,487; and Hung H. Bui, Reg. No. 40,415, my attorneys; of ANTONELLI, TERRY, STOUT & KRAUS, LLP with offices located at 1300 North Seventeenth Street, Suite 1800, Arlington, Virginia 22209, telephone: (703) 312-6600, fax: (703) 312-6666; with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith.

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TEL: (703) 312-6600
FAX: (703) 312-6666

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Inventor's Signature L. Döhring Date 26.3.02

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Title 37. Code of Federal Regulations, Section 1.56
Duty to Disclose Information Material to Patentability

(a) A patent by its very nature is affected with a public interest. The public interest is best served, and the most effective patent examination occurs when, at the time an application is being examined, the Office is aware of and evaluates the teachings of all information material to patentability. Each individual associated with the filing and prosecution of a patent application has a duty of candor and good faith in dealing with the Office, which includes a duty to disclose to the Office all information known to that individual to be material to patentability as defined in this section. The duty to disclosure information exists with respect to each pending claim until the claim is cancelled or withdrawn from consideration, or the application becomes abandoned. Information material to the patentability of a claim that is cancelled or withdrawn from consideration need not be submitted if the information is not material to the patentability of any claim remaining under consideration in the application. There is no duty to submit information which is not material to the patentability of any existing claim. The duty to disclosure all information known to be material to patentability is deemed to be satisfied if all information known to be material to patentability of any claim issued in a patent was cited by the Office or submitted to the Office in the manner prescribed by 991.97(b)-(d) and 1.98. However, no patent will be granted on an application in connection with which fraud on the Office was practiced or attempted or the duty of disclosure was violated through bad faith or intentional misconduct. The Office encourages applicants to carefully examine:

(1) Prior art cited in search reports of a foreign patent office in a counterpart application, and

(2) The closest information over which individuals associated with the filing or prosecution of a patent application believe any pending claim patentably defines, to make sure that any material information contained therein is disclosed to the Office.

(b) Under this section, information is material to patentability when it is not cumulative to information already of record or being made or record in the application, and

(1) It establishes, by itself or in combination with other information, a prima facie case of unpatentability of a claim; or

(2) It refutes, or is inconsistent with, a position the applicant takes in:

(i) Opposing an argument of unpatentability relied on by the Office, or

(ii) Asserting an argument of patentability.

A prima facie case of unpatentability is established when the information compels a conclusion that a claim is unpatentable under the preponderance of evidence, burden-of-proof standard, giving each term in the claim its broadest reasonable construction consistent with the specification, and before any consideration is given to evidence which may be submitted in an attempt to establish a contrary conclusion of patentability.

(c) Individuals associated with the filing or prosecution of a patent application within the meaning of this section are:

(1) Each inventor named in the application;

(2) Each attorney or agent who prepares or prosecutes the application; and

(3) Every other person who is substantively involved in the preparation or prosecution of the application and who is associated with the inventor, with the assignee or with anyone to whom there is an obligation to assign the application.

(d) Individuals other than the attorney, agent or inventor may comply with this section by disclosing information to the attorney, agent, or inventor.